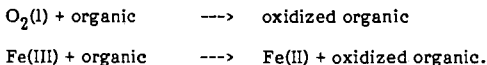### Enhanced Flue Gas Denitrification
Using Ferrous*EDTA and a Polyphenolic Compound
Having Combined Antioxidant and Reducing Properties

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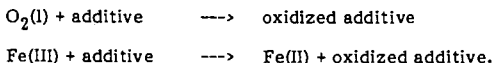Argonne National Laboratory, Argonne, IL 60439

ABSTRACT

Previous work in this laboratory has involved studying the possibility of combined NOx/SOx scrubbing using various aqueous chemistries with a metal chelate additive. Recently, we have focused our work on the metal chelate ferrous*EDTA. A major problem encountered in the practical application of ferrous*EDTA is that the ferrous ion has been found to oxidize to the corresponding ferric species leading to a decrease of the NOx removal for the scrubbing solution containing the additive. We have found that addition of a polyphenolic compound leads to a sustained high NOx removal under various oxidizing conditions. We believe that the improved performance of ferrous*EDTA is due to the known capabilities of these organic compounds to both inhibit oxidation of ferrous chelates by dissolved oxygen and to rapidly reduce any ferric ions back to the original ferrous species. These effects are illustrated by the chemical reactions shown below:

$$O_2(l) + organic \quad \longrightarrow \quad oxidized\ organic$$

$$Fe(III) + organic \quad \longrightarrow \quad Fe(II) + oxidized\ organic.$$

INTRODUCTION

The use of metal chelate additives in an aqueous scrubbing environment for combined NO_x/SO_2 removal from oxygen-containing flue gases has been investigated in this laboratory for several years (1,2,3). Recent work with the metal chelate Fe(II)*EDTA has shown initially high NO_x removals which, however, decline with time as a function of the amount of oxygen gas in the feed gas stream. Because of this dependence on oxygen concentration in the feed gas, we have attributed the decline in NO_x removal to the oxidation of the Fe(II)*EDTA additive to the ferric form. One possible solution to this problem would be to add a secondary additive to the system which is either capable of preferentially reacting with any dissolved oxygen or capable of reducing any oxidized ferric species back to the ferrous form. These chemical reactions may be summarized simply as follows:

$$O_2(l) + additive \quad \longrightarrow \quad oxidized\ additive$$

$$Fe(III) + additive \quad \longrightarrow \quad Fe(II) + oxidized\ additive.$$

From an examination of previous work in the literature, we have found one class of compounds which is capable of performing both of the above stated reactions. Theis and Singer (4) found that certain polyphenolic compounds, which are products of natural vegetative decay, are capable of significantly affecting the rate of oxidation of ferrous iron. This study showed, for example, that an equimolar amount of tannic acid was able to maintain a ferrous iron concentration of 5×10^{-5} M unchanged for 7 days in the presence of 0.5 atm O_2. Also phenols, such as gallic acid, are well-known antioxidants (5).

Because of the above stated properties of polyphenolic compounds, we have investigated the effect of tannic acid, pyrogallol, and gallic acid as secondary additives in aqueous scrubbing

systems containing the primary additive Fe(II)*EDTA. Using these secondary additives, we have been able to maintain NO_x removals as high as 60-65% for up to 2 hours.

EXPERIMENTAL SETUP

The complete experimental setup has been described previously (1,2). Some recent modifications to the scrubbing section have been made and are described herein. Figure 1 shows a flow diagram of the aqueous scrubber system that was used. One major modification is that a disk and donut scrubber having four (4) stages was used instead of the previously described flooded column. A sieve plate having 3/16" diameter holes with a total open area of 10.3% was placed at the bottom of the scrubber in order to provide the capability of having some liquid holdup in the column. Also, an approximately 10 liter holding tank was added to the system and connected to the bottom of the scrubber column. Circulation rates from the holding tank to the top of the scrubber could be varied from about 330-1420 ml/min. For the experiments described below, an average circulation rate of 890 ml/min was used. However, the circulation rate was varied in the range of 790-985 ml/min in order to maintain a fixed liquid level in the scrubber. All of the experiments discussed below were performed in a sodium, double-alkali chemistry by using a 0.31 M sodium carbonate solution.

Although the feed gas system is basically unchanged from that reported earlier (1,2), we have modified the procedure for preparing the simulated feed gas mixture. For the experiments to be reported, simulated feed gas was prepared by first setting the NO level at 450 ppm in the presence of carbon dioxide, oxygen, and nitrogen gases only. In all runs, the feed gas mixture contained 14.5% CO_2, 5.4% O_2, and N_2 as the balance. After the metering valve for the NO gas was set to give 450 ppm, a shut-off valve was closed and nitrogen dioxide was then set in the same CO_2, O_2, and N_2 mixture. Nitrogen dioxide is calculated as a difference between measured NO_x and measured NO and except where noted below was set around 75 ppm. The preset amount of NO was then added to the nitrogen dioxide. Finally, sulfur dioxide was added to the feed gas mixture and adjusted to the desired level. This new feed gas preparation procedure has improved the reproducibility and reliability of our removal measurements compared to the previously used method (1,2). Except where noted, approximately 8% water vapor was also added to the simulated feed gas mixture.

RESULTS AND CONCLUSIONS

We note that all experimental comparisons in this paper are made using total NO_x removal data. This is because we have observed that the presence (as in the feed stream) or absence (as in the effluent stream) of sulfur dioxide can alter the NO or (NO_x - NO) value, but has little effect on the total NO_x value. This "SO_2 effect" depends on the amount of unmixed nitrogen dioxide in the feed gas mixture and most likely arises from a gas phase reaction between SO_2 and NO_2. Because of the relatively small amount of NO_2 that we are adding in our new feed gas preparation procedure, as described above, this effect is small. In fact, although we still consider NO_x removals more reliable, in all cases discussed below, NO removals were never more than a few percent different from the reported NO_x removals.

We first present our initial experiment which was performed with tannic acid as the secondary additive using the previously described flooded column scrubber (1,2). Figure 2 shows NO_x removal for a baseline run with 0.24 moles of Fe(II)*EDTA alone versus that of an identical run with the addition of 0.04 moles of tannic acid. This first try experiment showed a significant improvement in NO_x removal from about 14% to about 40% in the stable portions of both curves. After this experiment, the scrubber column was changed from the flooded type to the disk and donut type described above.

Because of several problems with tannic acid, including the viscosity changes it caused, its high molecular weight, and its relatively high cost; we performed the remaining experiments with the polyphenolics pyrogallol and gallic acid. After trying several ferrous:polyphenolic

ratios, the most effective ratio was found to be approximately 1:1. This ratio of primary additive to secondary additive was used in all the experiments which follow.

Figure 3 compares NO_x removal for Fe(II)*EDTA alone versus that with pyrogallol as a secondary additive. This figure clearly demonstrates the declining NO_x removal with Fe(II)*EDTA alone versus the slightly increasing removal with pyrogallol. After 90 minutes, NO_x removal with pyrogallol was about twice that of Fe(II)*EDTA alone (64% vs 32%). The tests represented by this figure are the only ones in this paper which did not have moisture added to the feed gas stream. Figure 4 compares NO_x removals with pyrogallol for feed gas mixtures with and without added moisture. NO_x removal with added moisture was consistently about 6% greater than without added moisture. This effect is probably indicative of gas phase interactions of NO and/or NO_2 with water vapor as discussed earlier (1).

The next three figures illustrate the effect on NO_x removal of various changes in the feed gas stream composition. Figure 5 compares NO_x removals with pyrogallol for feed gas mixtures containing 1500 ppm and 3000 ppm sulfur dioxide. Although NO_x removal was 9% higher, on average, with 3000 ppm sulfur dioxide; it is interesting to note that after two hours of scrubbing with 1500 ppm SO_2, the NO_x removal had increased to about 56% with no apparent peak. Figure 6 compares NO_x removals for feed gas mixtures with 0 ppm versus 75 ppm NO_2 and 0 ppm versus 150 ppm NO_2, respectively. Figure 6a shows the removals were virtually identical for the first 90 minutes of each test; but for the last 30 minutes, the run with no NO_2 showed removal about 4% higher than the test with 75 ppm NO_2. Figure 6b shows that the test with 150 ppm NO_2 had slightly improved NO_x removal for the 10 - 90 minute interval (about 3%); but, again as in Figure 6a, the run with no NO_2 had a removal about 3% higher for the last 30 minutes. The point to be stressed here is that NO_2 levels of 0-150 ppm make relatively little difference on total NO_x removal.

Finally, Figure 7 compares NO_x removals for the secondary additives gallic acid and pyrogallol under identical conditions. While NO_x removal with pyrogallol was slightly better in the 20 to 80 minute interval (3% higher on average), after 80 minutes their performances were comparable.

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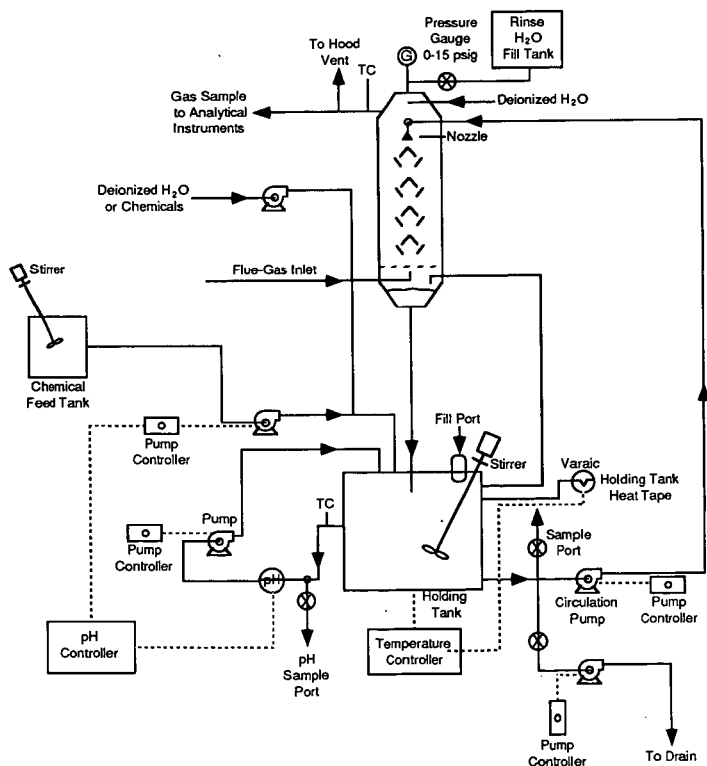5. Loginova, L.F., Medyntsev, V.V., and Khomutov, B.l., Zh. Obsh. Khim., 42, 739 (1972).

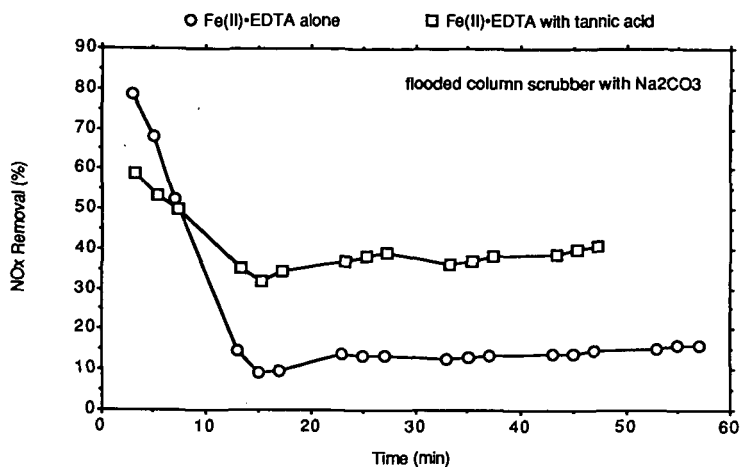Figure 1.   Flow diagram of laboratory aqueous scrubber system

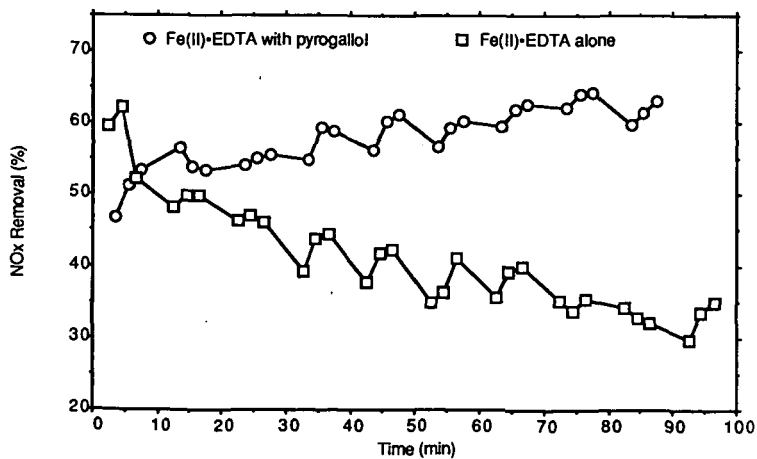Figure 2. NOx removal for Fe(II)·EDTA alone vs Fe(II)·EDTA with tannic acid

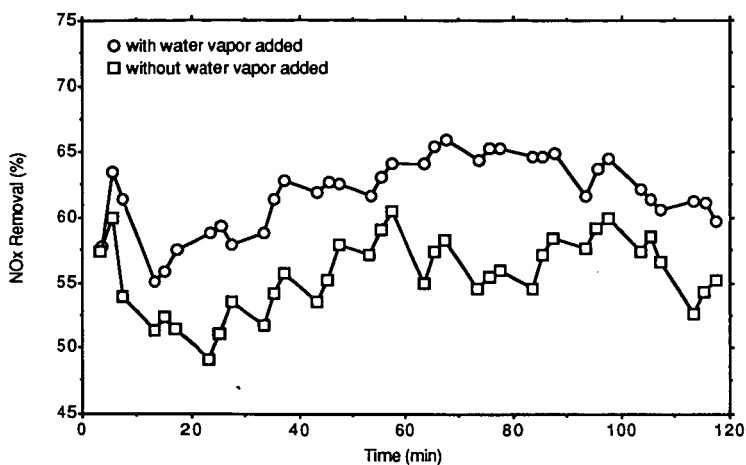Figure 3. Comparison of NOx removals with or without the secondary additive pyrogallol

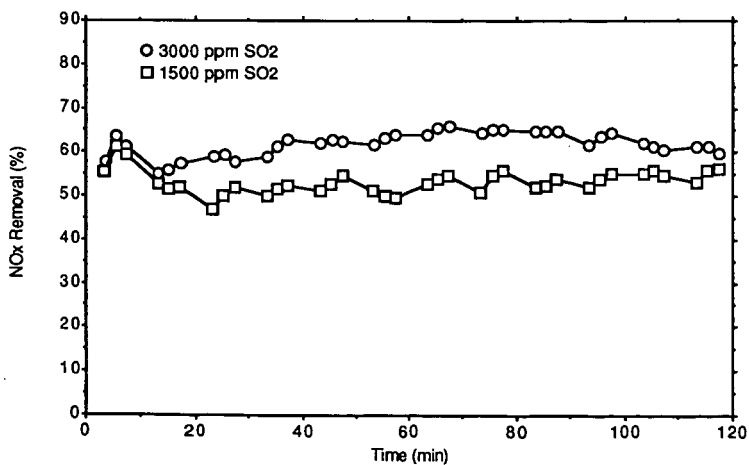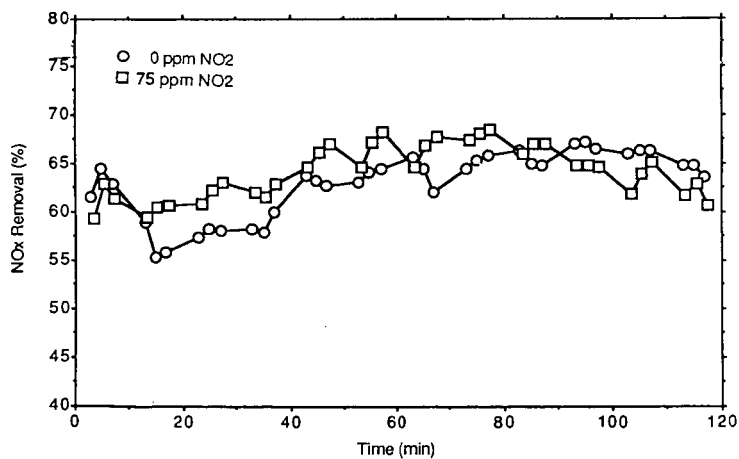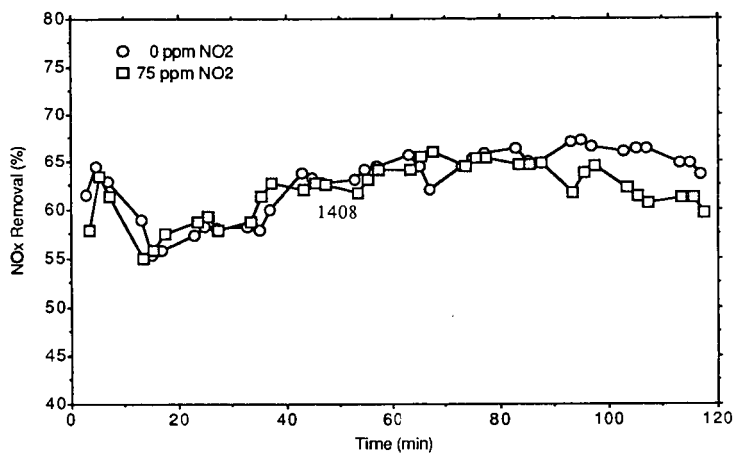Figure 4. Comparison of NOx removal for Fe(II)•EDTA and pyrogallol with or without moisture

Figure 5. Comparison of NOx removal for Fe(II)•EDTA and pyrogallol with different SO2 levels

Figures 6a. and b. Comparison of NOx removals for three different NO2 levels
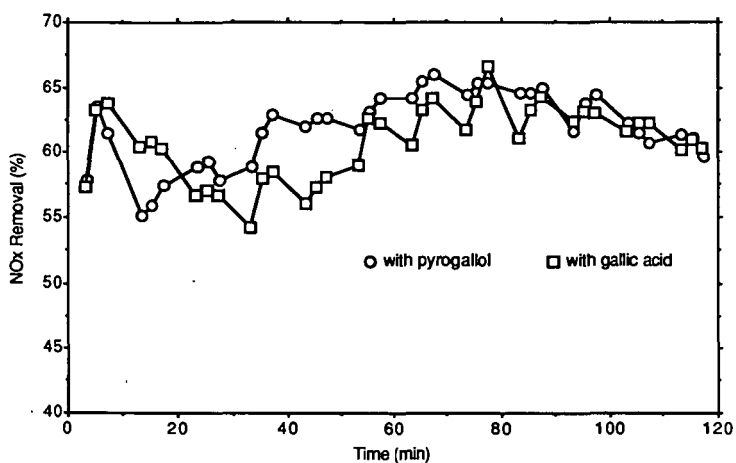
Figure 7. NOx removal comparison for secondary additives pyrogallol and gallic acid